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PYRETHROID MICROEMULSIONS AND THEIR USE

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(57) Claim

1. Stable pyrethroid microemulsions, characterised in that they comprise:

- from 0.1 % to 95 % by weight/weight of at least one synthetic pyrethroid in liquid form,
- from 2 % to 90 % by weight/weight of a surfactant system comprising:
  - . at least one anionic surfactant chosen from neutral phosphates or sulphates of alkoxylated di(1-phenylethyl)phenols or alkoxylated tri(1-phenylethyl)phenols, or alkali metal, alkaline earth metal, ammonium, alkylammonium and/or cycloalkylammonium or alkanolammonium alkylbenzenesulphonates,
  - . at least one nonionic surfactant chosen from:
    - + alkoxylated di(1-phenylethyl)phenols and alkoxylated tri(1-phenylethyl)phenols and
    - + ethoxypropoxylated nonylphenols;

.../2

. at least one co-surfactant chosen from:

+ straight-chain or branched aliphatic alcohols having from 3 to 10 carbon atoms,

+ cycloaliphatic alcohols having from 5 to 12 carbon atoms,

+ arylaliphatic alcohols having from 7 to 12 carbon atoms,

+ ether-alcohols of formula $R-(OR')_n-OH$ in which:

. R represents a straight-chain or branched alkyl radical having from 1 to 8 carbon atoms,

. R' represents an alkylene radical, and

. n represents an integer from 1 to 3, and

+ straight-chain or branched aliphatic carboxylic acids having from 5 to 10 carbon atoms,

- and water,

and in that the ratio by weight of anionic surfactant/nonionic surfactant is from 10/90 to 90/10, and the ratio by weight of co-surfactant/anionic and nonionic surfactants is from 0.1 to 1.5.

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COMPLETE SPECIFICATION

FOR A STANDARD PATENT

ORIGINAL

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Invention Title: "PYRETHROID MICROEMULSIONS AND THEIR USE"

The following statement is a full description of this invention, including the best method of performing it known to us:-

PYRETHROID MICROEMULSIONS AND THEIR USE

The present invention relates to new stable microemulsions and to their use for controlling insects, in particular in the treatment of crops and the protection of wood.

More precisely, it relates to stable pyrethroid microemulsions, characterised in that they comprise:

- from 0.1 % to 95 % by weight/weight of at least one pyrethroid in liquid form,
- from 2 % to 90 % by weight/weight of a surfactant system comprising:
  - . at least one anionic surfactant chosen from neutral phosphates or sulphates of alkoxylated di(1-phenylethyl)phenols or alkoxylated tri(1-phenylethyl)phenols, or alkali metal, alkaline earth metal, ammonium, alkylammonium and/or cycloalkylammonium or alkanolammonium alkylbenzenesulphonates,
  - . at least one nonionic surfactant chosen from:
    - + alkoxylated di(1-phenylethyl)phenols and alkoxylated tri(1-phenylethyl)phenols and
    - + ethoxypropoxylated nonylphenols;
  - . at least one co-surfactant chosen from:
    - + straight-chain or branched aliphatic alcohols having from 3 to 10 carbon atoms,
    - + cycloaliphatic alcohols having from 5 to 12 carbon atoms,

+ arylaliphatic alcohols having from 7 to 12 carbon atoms,

+ ether-alcohols of formula $R-(OR')_n-OH$ in which:

. R represents a straight-chain or branched alkyl radical having from 1 to 8 carbon atoms,

. R' represents an alkylene radical, such as ethylene or propylene, and

. n represents an integer from 1 to 3, and

+ straight-chain or branched aliphatic carboxylic acids having from 5 to 10 carbon atoms,

- and water,

and in that the ratio by weight of anionic surfactant/nonionic surfactant is from 10/90 to 90/10, and the ratio by weight of co-surfactant/anionic and nonionic surfactants is from 0.1 to 1.5.

Pyrethroids are insecticidal active compounds which may be used, in particular, in the plant protection field or in the protection of wood.

The following may be mentioned amongst the best known:

- allethrin
- bifenthrin
- bioallethrin
- bioresmethrin
- cyfluthrin

- cyhallothrin
- cypermethrin
- deltamethrin
- fenpropathrin
- permethrin
- phenothrin
- pyrethrins
- resmethrin
- tefluthrin
- tetramethrin
- tralomethrin
- (E)-5-benzy-3-furylmethyl (1R)-cis-2,2-dimethyl-3-(2-oxothiolan-3-ylidene-methyl)cyclopropanecarboxylate [sic].

The pyrethroids may be used as such, in particular those which are liquid at ambient temperature, that is to say at about 10 to 25°C, or those which may be supercooled.

It is also possible to use the pyrethroids in solution in an organic solvent insoluble in water (or in a mixture of such organic solvents), in particular the pyrethroids which have a melting point higher than about 50°C, without this temperature being a critical limit.

The following may be mentioned as examples of organic solvents which enable the pyrethroids to be preserved in the liquid state: aromatic hydrocarbons, such as benzene, toluene or xylenes; aromatic petroleum

cuts; fatty acid alkyl esters, such as methyl oleate; dialkyl phthalates, such as di(2-ethylhexyl) phthalate; chlorinated hydrocarbons, such as dichloromethane, trichloromethane or 1,2-chloroethane; and cyclic ketones, such as cyclopentanone, cyclohexanone or isophorone.

When an organic solvent is used, the ratio by weight of organic solvent/pyrethroid may vary widely from 5/95 to 90/10.

In the present text the term "pyrethroid in liquid form" thus encompasses liquid, supercooled or dissolved pyrethroids. In this latter case, the amounts of pyrethroid expressed in the formulations comprise both the pyrethroid itself and the solvent which contains it.

One pyrethroid or a mixture of several pyrethroids may be used in the microemulsions of the invention.

Amongst the anionic surfactants used in the pyrethroid microemulsions, the following may be mentioned more particularly:

- phosphoric monoesters and diesters of ethoxylated di(1-phenylethyl)phenols containing from 2 to 50 ethylene oxide (EO) units,
- phosphoric monoesters and diesters of ethoxylated tri(1-phenylethyl)phenols containing from 2 to 50 EO units,
- phosphoric monoesters and diesters of

propoxylated di(1-phenylethyl)phenols containing from 2 to 50 propylene oxide (PO) units,

- phosphoric monoesters and diesters of propoxylated tri(1-phenylethyl)phenols containing from 2 to 50 PO units,

- phosphoric monoesters and diesters of ethoxypropoxylated di(1-phenylethyl phenols [sic] containing from 2 to 50 EO + PO units,

- phosphoric monoesters and diesters of ethoxypropoxylated tri(1-phenylethyl)phenols containing from 2 to 50 EO + PO units,

- sulphuric monoesters and diesters of ethoxylated di(1-phenylethyl)phenols containing from 2 to 50 EO units,

- sulphuric monoesters and diesters of propoxylated di(1-phenylethyl)phenols containing from 2 to 50 PO units,

- sulphuric monoesters and diesters of ethoxypropoxylated di(1-phenylethyl)phenols containing from 2 to 50 EO + PO units,

- sulphuric monoesters and diesters of ethoxylated tri(1-phenylethyl)phenols containing from 2 to 50 EO units,

- sulphuric monoesters and diesters of propoxylated tri(1-phenylethyl)phenols containing from 2 to 50 PO units, and

- sulphuric monoesters and diesters of ethoxypropylated [sic] tri(1-phenylethyl)phenols

containing from 2 to 50 EO + PO units,

in which any free acid functions are neutralised by alkanolamines or ammonium, potassium or sodium cations, and

- sodium, potassium, calcium, ammonium, diethanolammonium, triethanolammonium and N-methylcyclohexylammonium nonylbenzenesulphonates and dodecylbenzenesulphonates.

Examples of anionic surfactants which may be mentioned in a non-limiting manner are some compounds such as:

- triethanolamine salts of the phosphoric monoester and diester of ethoxylated tri(1-phenylethyl)phenol containing 16 EO units,
- the potassium salts of the phosphoric monoester and diester of ethoxylated tri(1-phenylethyl)phenol containing 16 EO units,
- the potassium salt of the sulphuric monoester of the ethoxylated di(1-phenylethyl)phenol containing 15 EO units,
- the triethanolamine salt of the sulphuric monoester of ethoxylated di(1-phenylethyl)phenol containing 11 EO units,
- the ammonium salt of the sulphuric monoester of ethoxylated tri(1-phenylethyl)phenol containing 16 EO units,
- the ammonium salt of the sulphuric monoester of ethoxylated di(1-phenylethyl)phenol

containing 5 EO units,

- the ammonium salt of the sulphuric monoester of ethoxylated di(1-phenylethyl)phenol containing 7 EO units,
- the ammonium salt of the sulphuric monoester of ethoxylated di(1-phenylethyl)phenol containing 11 EO units,
- calcium dodecylbenzenesulphonate,
- ammonium dodecylbenzenesulphonate,
- sodium dodecylbenzenesulphonate,
- potassium dodecylbenzenesulphonate, and
- triethanolammonium dodecylbenzenesulphonate.

It is, of course, possible to use mixtures of several anionic surfactants without departing from the scope of the invention.

Amongst the nonionic surfactants used in the microemulsions, the following may be mentioned more particularly:

- ethoxylated di(1-phenylethyl)phenols containing from 2 to 50 EO units,
- propoxylated di-1-phenylethyl)phenols [sic] containing from 2 to 50 PO units,
- ethoxypropoxylated di(1-phenylethyl)-phenols containing from 2 to 50 EO + PO units,
- ethoxylated tri(1-phenylethyl)phenols containing from 2 to 50 EO units,
- propoxylated tri(1-phenylethyl)phenols

containing from 2 to 50 PO units,

- ethoxypropoxylated tri(1-phenylethyl)-phenols containing from 2 to 50 EO + PO units, and
- ethoxypropoxylated nonylphenols containing 2 to 100 EO + PO units.

Examples of nonionic surfactants which may be mentioned in a non-limiting manner are some compounds such as:

- ethoxypropoxylated nonylphenols having 25 EO + PO units,
- ethoxypropoxylated nonylphenols having 30 EO + PO units,
- ethoxypropoxylated nonylphenols having 40 EO + PO units,
- ethoxypropoxylated nonylphenols having 55 EO + PO units,
- ethoxypropoxylated nonylphenols having 80 EO + PO units,
- ethoxypropoxylated tri(1-phenylethyl)-phenols having 25 EO + PO units,
- ethoxylated tri(1-phenylethyl)phenol having 16 EO units,
- ethoxylated tri(1-phenylethyl)phenol having 20 EO units,
- ethoxylated tri(1-phenylethyl)phenol having 25 EO units,
- ethoxylated tri(1-phenylethyl)phenol having 40 EO units,

- ethoxylated di(1-phenylethyl)phenol having 5 EO units,

- ethoxylated di(1-phenylethyl)phenol having 11 EO units, and

- ethoxylated di(1-phenylethyl)phenol having 15 EO units.

As in the case of the anionic surfactants, mixtures of several nonionic surfactants may be used without departing from the scope of the invention.

When the anionic surfactant is an alkylbenzenesulphonate as defined above, the nonionic surfactant is preferably chosen from alkoxylated di(1-phenylethyl)phenols and alkoxylated tri(1-phenylethyl)phenols.

Amongst the co-surfactants, the following may be mentioned in a non-limiting manner: n-butanol, isobutanol (butan-2-ol), n-propanol, isopropanol (propan-2-ol), n-pentanol and its branched isomers, n-hexanol and its branched isomers, cyclopentanol, cyclohexanol, methylcyclohexanols, benzyl alcohol, phenylethyl alcohol, 2-methoxyethanol, 2-ethoxyethanol, 2-isopropoxyethanol, 2-n-butoxyethanol, diethylene glycol monomethyl ether, diethylene glycol monoethyl ether, diethylene glycol mono-n-butyl ether, triethylene glycol monoethyl ether, heptanoic acid and its branched isomers, octanoic acid and its branched isomers, nonanoic acid and its branched isomers and decanoic acid and its branched isomers.

It is also possible to use mixtures of co-surfactants.

In general, it will be preferred to use co-surfactants having a flash point higher than 50°C.

The flash point is defined as the temperature above which the vapours of the product ignite spontaneously in contact with a flame.

Preferably, the microemulsions according to the invention comprise:

- from 0.1 % to 70 % by weight of at least one pyrethroid in liquid form, and
- from 2 % to 50 % by weight of a surfactant system comprising at least one anionic surfactant, at least one nonionic surfactant and at least one co-surfactant, in which the ratio by weight of anionic surfactant/nonionic surfactant is from 15/85 to 85/15 and the ratio by weight of co-surfactant/anionic and nonionic surfactants is from 0.25 to 0.80.

The microemulsions according to the invention may contain, in addition to the compounds defined above, other compounds customary in plant protection compositions, such as anti-foams, such as organopolysiloxanes, thickeners, such as xanthan gum, preservatives and an antigel, such as monopropylene glycol or monoethylene glycol.

The microemulsions according to the invention are stable in a temperature range of from -5°C to

+45°C.

The microemulsions are prepared by simple mixing of the various constituents.

They do not give rise to any coalescence, crystallisation or sedimentation phenomenon on storage.

They may be used to control insects, in particular in the treatment of crops or the protection of wood, either directly or after dilution with water at the time of their use. On dilution, they lead to stable emulsions or microemulsions. In the plant protection field, the dilute emulsions or microemulsions are prepared by the user at the time of use and are not generally stored for more than 24 hours.

The following examples illustrate the invention.

EXAMPLE 1:

A microemulsion is prepared by mixing the following compounds, with stirring:

- cypermethrin: 10.90 g
- ethoxylated tri(1-phenylethyl)phenol containing 16 EO units: 15.34 g
- ethoxylated tri(1-phenylethyl)phenol phosphate containing 16 EO units and neutralised by triethanolamine: 8.26 g
- isobutanol: 11.80 g
- water (to make up to 100 g): 53.70 g

A microemulsion is obtained which is clear,

(by definition) fluid and stable under a temperature cycle of -5°C, +45°C.

EXAMPLE 2:

Example 1 is repeated using the following compounds:

- cypermethrin: 27.90 g
- ethoxylated tri(1-phenylethyl)phenol containing 16 EO units: 18.64 g
- ethoxylated tri(1-phenylethyl)phenol phosphate containing 16 EO units and neutralised by triethanolamine: 10.03 g
- isobutanol: 14.33 g
- water (to make up to 100 g): 29.10 g

A microemulsion is obtained which is clear, fluid and stable under a temperature cycle of -5°C, +45°C.

EXAMPLE 3:

Example 1 is repeated using the following compounds:

- cypermethrin: 9.40 g
- ethoxylated tri(1-phenylethyl)phenol containing 16 EO units: 14.26 g
- ethoxylated tri(1-phenylethyl)phenol phosphate containing 16 EO units and neutralised by triethanolamine: 7.68 g
- cyclohexanol: 16.46 g
- water (to make up to 100 g): 52.20 g

A microemulsion is obtained which is clear,

fluid and stable under a temperature cycle of -5°C, +45°C.

EXAMPLE 4:

Example 1 is repeated using the following compounds:

- cypermethrin: 26.10 g
- ethoxylated tri(1-phenylethyl)phenol containing 16 EO units: 25.63 g
- ethoxylated tri(1-phenylethyl)phenol phosphate containing 16 EO units and neutralised by triethanolamine: 13.80 g
- cyclohexanol: 29.57 g
- water (to make up to 100 g): 4.90 g

A microemulsion is obtained which is clear, fluid and stable under a temperature cycle of -5°C, +45°C.

EXAMPLE 5:

Example 1 is repeated using the following compounds:

- cypermethrin: 9.0 g
- ethoxylated di(1-phenylethyl)phenol containing 15 EO units: 33.98 g
- ethoxylated di(1-phenylethyl)phenol sulphate containing 15 EO units and neutralised by KOH: 18.30 g
- isobutanol: 26.14 g
- water (to make up to 100 g): 12.58 g

A microemulsion is obtained which is clear,

fluid and stable under a temperature cycle of -5°C, +45°C.

EXAMPLE 6:

Example 1 is repeated using the following compounds:

- cypermethrin: 23.0 g
- ethoxylated di(1-phenylethyl)phenol containing 15 EO units: 25.52 g
- ethoxylated di(1-phenylethyl)phenol sulphate containing 15 EO units and neutralised by KOH: 13.74 g
- isobutanol: 19.64 g
- water (to make up to 100 g): 18.10 g

A microemulsion is obtained which is clear, fluid and stable under a temperature cycle of -5°C, +45°C.

EXAMPLE 7:

Example 1 is repeated using the following compounds:

- permethrin: 9.03 g
- ethoxylated tri(1-phenylethyl)phenol containing 16 EO units: 20.11 g
- ethoxylated tri(1-phenylethyl)phenol phosphate containing 16 EO units and neutralised by triethanolamine: 10.83 g
- isobutanol: 15.46 g
- water (to make up to 100 g): 44.57 g

A microemulsion is obtained which is clear,

fluid and stable under a temperature cycle of -5°C, +45°C.

EXAMPLE 8:

Example 1 is repeated using the following compounds:

- permethrin: 26.80 g
- ethoxylated tri(1-phenylethyl)phenol containing 16 EO units: 18.46 g
- ethoxylated tri(1-phenylethyl)phenol phosphate containing 16 EO units and neutralised by triethanolamine: 9.94 g
- isobutanol: 14.20 g
- water (to make up to 100 g): 30.60 g

A microemulsion is obtained which is clear, fluid and stable under a temperature cycle of -5°C, +45°C.

EXAMPLE 9:

Example 1 is repeated using the following compounds:

- cypermethrin: 27.60 g
- ethoxylated tri(1-phenylethyl)phenol containing 16 EO units: 22.95 g
- ethoxylated tri(1-phenylethyl)phenol phosphate containing 16 EO units and neutralised by triethanolamine: 12.36 g
- cyclohexanol: 26.49 g
- water (to make up to 100 g): 10.60 g

A microemulsion is obtained which is clear,

fluid and stable under a temperature cycle of -5°C, +45°C.

EXAMPLE 10:

Example 1 is repeated using the following compounds:

- deltamethrin: 8.70 g
- aromatic petroleum cut (Solvesso 150): 28.40 g
- cyclohexanone: 15.20 g
- ethoxylated tri(1-phenylethyl)phenol containing 16 EO units: 13.50 g
- ethoxylated tri(1-phenylethyl)phenol sulphate containing 16 EO units and neutralised by NH_3: 7.30 g
- cyclohexanol: 13.90 g
- monopropylene glycol: 2.60 g
- water (to make up to 100 g): 10.40 g

A microemulsion is obtained which is clear, fluid and stable under a temperature cycle of -5°C, +45°C.

EXAMPLE 11:

Example 1 is repeated using the following compounds:

- permethrin: 42.30 g
- ethoxylated tri(1-phenylethyl)phenol containing 16 EO units: 17.16 g
- ethoxylated tri(1-phenylethyl)phenol phosphate containing 16 EO units and neutralised by triethanolamine: 9.24 g

- cyclohexanol: 20.0 g
- water (to make up to 100 g): 11.30 g

A microemulsion is obtained which is clear, fluid and stable under a temperature cycle of -5°C, +45°C.

EXAMPLE 12:

Example 1 is repeated using the following compounds:

- cypermethrin: 48.6 g
- ethoxylated tri(1-phenylethyl)phenol containing 16 EO units: 15.50 g
- ethoxylated tri(1-phenylethyl)phenol phosphate containing 16 EO units and neutralised by triethanolamine: 8.30 g
- cyclohexanol: 18.0 g
- water (to make up to 100 g): 9.60 g

A microemulsion is obtained which is clear, fluid and stable under a temperature cycle of -5°C, +45°C.

EXAMPLE 13:

Example 1 is repeated using the following compounds:

- cypermethrin: 45.6 g
- ethoxylated tri(1-phenylethyl)phenol containing 25 EO units: 6.0 g
- ethoxylated tri(1-phenylethyl)phenol phosphate containing 16 EO units and neutralised by triethanolamine: 24.0 g

- isobutanol: 14.8 g
- water (to make up to 100 g): 9.6 g

A microemulsion is obtained which is clear, fluid and stable under a temperature cycle of -5°C, +45°C.

EXAMPLE 14:

Example 1 is repeated using the following compounds:

- cypermethrin: 47.3 g
- ethoxylated tri(1-phenylethyl)phenol containing 16 EO units: 15.9 g
- ethoxylated di(1-phenylethyl)phenol sulphate containing 15 EO units and neutralised by KOH: 10.14 g
- isobutanol: 14.52 g
- water (to make up to 100 g): 12.14 g

A microemulsion is obtained which is clear, fluid and stable under a temperature cycle of -5°C, +45°C.

EXAMPLE 15:

Example 1 is repeated using the following compounds:

- cypermethrin: 47.3 g
- ethoxylated tri(1-phenylethyl)phenol containing 16 EO units: 21.7 g
- calcium dodecylbenzenesulphonate: 13.0 g
- isobutanol: 8.7 g
- water (to make up to 100 g): 9.3 g

A microemulsion is obtained which is clear, fluid and stable under a temperature cycle of -5°C, +45°C.

EXAMPLE 16:

Example 1 is repeated using the following compounds:

- cypermethrin: 28.0 g
- ethoxylated tri(1-phenylethyl)phenol containing 16 EO units: 10.27 g
- ethoxylated tri(1-phenylethyl)phenol phosphate containing 16 EO units and neutralised by KOH: 19.06 g
- isobutanol: 14.67 g
- water (to make up to 100 g): 28.0 g

A microemulsion is obtained which is clear, fluid and stable under a temperature cycle of -5°C, +45°C.

EXAMPLE 17:

Example 1 is repeated using the following compounds:

- cypermethrin: 28.0 g
- ethoxylated tri(1-phenylethyl)phenol containing 16 EO units: 10.27 g
- ethoxylated tri(1-phenylethyl)phenol phosphate containing 16 EO units and neutralised by NH_3: 19.06 g
- isobutanol: 14.67 g
- water (to make up to 100 g): 28.0 g

A microemulsion is obtained which is clear, fluid and stable under a temperature cycle of -5°C, +45°C.

COMPARATIVE EXPERIMENT A:

Example 1 is repeated using the following compounds:

- cypermethrin: 28.0 g
- ethoxylated tri(1-phenylethyl)phenol containing 16 EO units: 10.27 g
- ethoxylated tri(1-phenylethyl)phenol phosphate containing 16 EO units in acid form: 19.06 g
- isobutanol: 14.67 g
- water (to make up to 100 g): 28.0 g

A microemulsion is obtained which is clear, fluid and stable at 20°C but unstable when it is subjected to heat cycles in the temperature zone of -5°C, +45°C.

EXAMPLE 18:

Example 1 is repeated using the following compounds:

- cypermethrin: 58.0 g
- ethoxylated tri(1-phenylethyl)phenol containing 16 EO units: 8.17 g
- ethoxylated tri(1-phenylethyl)phenol phosphate containing 16 EO units and neutralised by KOH: 15.16 g
- isobutanol: 11.67 g

- water (to make up to 100 g): 7.0 g

A microemulsion is obtained which is clear, fluid and stable under a te..perature cycle of -5°C, +45°C.

EXAMPLE 19:

Example 1 is repeated using the following compounds:

- cypermethrin: 58.0 g
- ethoxylated tri(1-phenylethyl)phenol containing 16 EO units: 8.17 g
- ethoxylated tri(1-phenylethyl)phenol phosphate containing 16 EO units and neutralised by NH_3: 15.16 g
- isobutanol: 11.67 g
- water (to make up to 100 g): 7.0 g

A microemulsion is obtained which is clear, fluid and stable under a temperature cycle of -5°C, +45°C.

COMPARATIVE EXPERIMENT B:

Example 1 is repeated using the following compounds:

- cypermethrin: 58.0 g
- ethoxylated tri(1-phenylethyl)phenol containing 16 EO units: 8.17 g
- ethoxylated tri(1-phenylethyl)phenol phosphate containing 16 EO units in acid form: 15.16 g
- isobutanol: 11.67 g

- water (to make up to 100 g): 7.0 g

A microemulsion is obtained which is clear, fluid and stable at 20°C but unstable when it is subjected to heat cycles in the temperature zone of -5°C, +45°C.

EXAMPLE 20:

Example 1 is repeated using the following compounds:

- cypermethrin: 8.0 g
- ethoxylated tri(1-phenylethyl)phenol containing 16 EO units: 7.23 g
- ethoxylated tri(1-phenylethyl)phenol phosphate containing 16 EO units and neutralised by KOH: 13.43 g
- isobutanol: 10.34 g
- water (to make up to 100 g): 61.0 g

A microemulsion is obtained which is clear, fluid and stable under a temperature cycle of -5°C, +45°C.

EXAMPLE 21:

Example 1 is repeated using the following compounds:

- cypermethrin: 8.0 g
- ethoxylated tri(1-phenylethyl)phenol containing 16 EO units: 7.23 g
- ethoxylated tri(1-phenylethyl)phenol phosphate containing 16 EO units and neutralised by NH_3: 13.43 g

- isobutanol: 10.34 g
- water (to make up to 100 g): 61.0 g

A microemulsion is obtained which is clear, fluid and stable under a temperature cycle of -5°C, +45°C.

COMPARATIVE EXPERIMENT C:

Example 1 is repeated using the following compounds:

- cypermethrin: 8.0 g
- ethoxylated tri(1-phenylethyl)phenol containing 16 EO units: 7.23 g
- ethoxylated tri(1-phenylethyl)phenol phosphate containing 16 EO units in acid form: 13.43 g
- isobutanol: 10.34 g
- water (to make up to 100 g): 61.0 g

A microemulsion is obtained which is clear, fluid and stable at 20°C but unstable when it is subjected to heat cycles in the temperature zone of -5°C, +45°C.

EXAMPLE 22:

Example 1 is repeated using the following compounds:

- cypermethrin: 8.0 g
- ethoxylated tri(1-phenylethyl)phenol containing 16 EO units: 10.13 g
- ethoxylated tri(1-phenylethyl)phenol sulphate containing 16 EO units and

neutralised by NH_3: 10.13 g

- isobutanol: 10.13 g
- water (to make up to 100 g): 61.61 g

A microemulsion is obtained which is clear, fluid and stable under a temperature cycle of -5°C, +45°C.

COMPARATIVE EXPERIMENT D:

Example 1 is repeated using the following compounds:

- cypermethrin: 8.0 g
- ethoxylated nonylphenol containing 10 EO units: 10.13 g
- ethoxylated tri(1-phenylethyl)phenol sulphate containing 16 EO units and neutralised by NH_3: 10.13 g
- isobutanol: 10.13 g
- water (to make up to 100 g): 61.61 g

A microemulsion is obtained which is clear, fluid and stable at 20°C but unstable when it is subjected to heat cycles in the temperature zone of -5°C, +45°C.

COMPARATIVE EXPERIMENT E:

Example 1 is repeated using the following compounds:

- cypermethrin: 8.0 g
- ethoxylated nonylphenol containing 17 EO units: 10.13 g
- ethoxylated tri(1-phenylethyl)phenol

sulphate containing 16 EO units and neutralised by NH_3: 10.13 g

- isobutanol: 10.13 g
- water (to make up to 100 g): 61.61 g

A microemulsion is obtained which is clear, fluid and stable at 20°C but unstable when it is subjected to heat cycles in the temperature zone of -5°C, +45°C.

EXAMPLE 23:

Example 1 is repeated using the following compounds:

- cypermethrin: 28.0 g
- ethoxylated tri(1-phenylethyl)phenol containing 16 EO units: 14.67 g
- ethoxylated tri(1-phenylethyl)phenol sulphate containing 16 EO units and neutralised by NH_3: 14.67 g
- isobutanol: 14.66 g
- water (to make up to 100 g): 28.0 g

A microemulsion is obtained which is clear, fluid and stable under a temperature cycle of -5°C, +45°C.

COMPARATIVE EXPERIMENT F:

Example 1 is repeated using the following compounds:

- cypermethrin: 28.0 g
- ethoxylated nonylphenol containing 10 EO units: 14.67 g

- ethoxylated tri(1-phenylethyl)phenol sulphate containing 16 EO units and neutralised by NH_3: 14.67 g
- isobutanol: 14.66 g
- water (to make up to 100 g): 28.0 g

A microemulsion is obtained which is clear, fluid and stable at 20°C but unstable when it is subjected to heat cycles in the temperature zone of -5°C, +45°C.

COMPARATIVE EXPERIMENT G:

Example 1 is repeated using the following compounds:

- cypermethrin: 28.0 g
- ethoxylated nonylphenol containing 17 EO units: 14.67 g
- ethoxylated tri(1-phenylethyl)phenol sulphate containing 16 EO units and neutralised by NH_3: 14.67 g
- isobutanol: 14.66 g
- water (to make up to 100 g): 28.0 g

A microemulsion is obtained which is clear, fluid and stable at 20°C but unstable when it is subjected to heat cycles in the temperature zone of -5°C, +45°C.

THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS:

1. Stable pyrethroid microemulsions, characterised in that they comprise:

- from 0.1 % to 95 % by weight/weight of at least one synthetic pyrethroid in liquid form,
- from 2 % to 90 % by weight/weight of a surfactant system comprising:
  - . at least one anionic surfactant chosen from neutral phosphates or sulphates of alkoxylated di(1-phenylethyl)phenols or alkoxylated tri(1-phenylethyl)phenols, or alkali metal, alkaline earth metal, ammonium, alkylammonium and/or cycloalkylammonium or alkanolammonium alkylbenzenesulphonates,
  - . at least one nonionic surfactant chosen from:
    - + alkoxylated di(1-phenylethyl)phenols and alkoxylated tri(1-phenylethyl)phenols and
    - + ethoxypropoxylated nonylphenols;
  - . at least one co-surfactant chosen from:
    - + straight-chain or branched aliphatic alcohols having from 3 to 10 carbon atoms,
    - + cycloaliphatic alcohols having from 5 to 12 carbon atoms,
    - + arylaliphatic alcohols having from 7 to 12 carbon atoms,
    - + ether-alcohols of formula $R-(OR')_n-OH$ in which:
      - . R represents a straight-chain or branched

alkyl radical having from 1 to 8 carbon atoms,

. R' represents an alkylene radical, and

. n represents an integer from 1 to 3, and

+ straight-chain or branched aliphatic carboxylic acids having from 5 to 10 carbon atoms,

- and water,

and in that the ratio by weight of anionic surfactant/nonionic surfactant is from 10/90 to 90/10, and the ratio by weight of co-surfactant/anionic and nonionic surfactants is from 0.1 to 1.5.

2. Microemulsion according to claim 1 wherein R' is an ethylene or propylene.

3. Microemulsion according to claim 1 or 2, characterised in that the pyrethroids are insecticidal active compounds chosen from:

- allethrin
- bifenthrin
- bioallethrin
- bioresmethrin
- cyfluthrin
- cyhallothrin
- cypermethrin
- deltamethrin
- fenpropathrin
- permethrin
- phenothrin
- pyrethrins
- resmethrin
- tefluthrin

- tetramethrin
- tralomethrin
- (E)-5-benzyl-3-furylmethyl (1R)-cis-2,2-dimethyl-3-(2-oxothiolan-3-ylidene-methyl) cyclopropanecarboxylate.

4. Microemulsion according to any one of claims 1 to 3, characterised in that the pyrethroids used are those which are liquid at ambient temperature or those which may be supercooled.

5. Microemulsion according to any one of claims 1 to 4, characterised in that the pyrethroids used are in solution in an organic solvent insoluble in water.

6. Microemulsion according to claim 5, characterised in that the organic solvent, enabling the pyrethroids to be preserved in the liquid state, is chosen from aromatic hydrocarbons; aromatic petroleum cuts; fatty acid alkyl esters; dialkyl phthalates; chlorinated hydrocarbons; and cyclic ketones.

7. Microemulsion according to claim 6, characterised in that the aromatic hydrocarbon is benzene, toluene or xylene.

8. Microemulsion according to claim 6, characterised in that the fatty acid alkyl ester is methyl oleate.

9. Microemulsion according to claim 6, characterised in that the dialkyl phthalate is di(2-ethylhexyl)phthalate.

10. Microemulsion according to claim 6, characterised in that the chlorinated hydrocarbon is dichloromethane, trichloromethane or 1,2-chloroethane.

11. Microemulsion according to claim 6, characterised in that the cyclic ketone is cyclopentanone, cyclohexanone or isophorone.

12. Microemulsion according to any one of claims 4 to 11, characterised in that the ratio by weight of organic solvent/pyrethroid varies from 5/95 to 90/10.

13. Microemulsion according to any one of claims 1 to 12, characterised in that the anionic surfactants used are chosen from:

- phosphoric monoesters and diesters of ethoxylated di(1-phenylethyl)phenols containing from 2 to 50 ethylene oxide (EO) units,
- phosphoric monoesters and diesters of ethoxylated tri(1-phenylethyl)phenols containing from 2 to 50 EO units,
- phosphoric monoesters and diesters of propoxylated di(1-phenylethyl)phenols containing from 2 to 50 propylene oxide (PO) units,
- phosphoric monoesters and diesters of propoxylated tri(1-phenylethyl)phenols containing from 2 to 50 PO units,
- phosphoric monoesters and diesters of ethoxypropoxylated di(1-phenylethyl)phenols containing from 2 to 50 EO + PO units,
- phosphoric monoesters and diesters of ethoxypropoxylated tri(1-phenylethyl)phenols containing from 2 to 50 EO + PO units,
- sulphuric monoesters and diesters of ethoxylated di(1-phenylethyl)phenols containing from 2 to 50 EO units,

- sulphuric monoesters and diesters of propoxylated di(1-phenylethyl)phenols containing from 2 to 50 PO units,
- sulphuric monoesters and diesters of ethoxypropoxylated di(1-phenylethyl)phenols containing from 2 to 50 EO + PO units,
- sulphuric monoesters and diesters of ethoxylated tri(1-phenylethyl)phenols containing from 2 to 50 EO units,
- sulphuric monoesters and diesters of propoxylated tri(1-phenylethyl)phenols containing from 2 to 50 PO units, and
- sulphuric monoesters and diesters of ethoxypropoxylated tri(1-phenylethyl)phenols containing from 2 to 50 EO + PO units, in which any free acid functions are neutralised by alkanolamines or ammonium, potassium or sodium cations, and
- sodium, potassium, calcium, ammonium, diethanolammonium, triethanolammonium and N-methylcyclohexylammonium nonylbenzenesulphonates and dodecylbenzenesulphonates.

14. Microemulsion according to any one of claims 1 to 13, characterised in that the anionic surfactants used are chosen from:

- triethanolamine salts of the phosphoric monoester and diester of ethoxylated tri(1-phenylethyl)phenol containing 16 EO units,
- the potassium salts of the phosphoric monoester and diester of ethoxylated tri(1-phenylethyl)phenol containing 16 EO units,

- the potassium salt of the sulphuric monoester of the ethoxylated di(1-phenylethyl)phenol containing 15 EO units,
- the triethanolamine salt of the sulphuric monoester of ethoxylated di(1-phenylethyl)phenol containing 11 EO units,
- the ammonium salt of the sulphuric monoester of ethoxylated tri(1-phenylethyl)phenol containing 16 EO units,
- the ammonium salt of the sulphuric monoester of ethoxylated di(1-phenylethyl)phenol containing 5 EO units,
- the ammonium salt of the sulphuric monoester of ethoxylated di(1-phenylethyl)phenol containing 7 EO units,
- the ammonium salt of the sulphuric monoester of ethoxylated di(1-phenylethyl)phenol containing 11 EO units,
- calcium dodecylbenzenesulphonate,
- ammonium dodecylbenzenesulphonate,
- sodium dodecylbenzenesulphonate,
- potassium dodecylbenzenesulphonate, and
- triethanolammonium dodecylbenzenesulphonate.

15. Microemulsion according to any one of claims 1 to 14, characterised in that the nonionic surfactants used are chosen from:

- ethoxylated di(1-phenylethyl)phenols containing from 2 to 50 EO units,
- propoxylated di(1-phenylethyl)phenols containing from 2 to 50 PO units,
- ethoxypropoxylated di(1-phenylethyl)phenols

containing from 2 to 50 EO + PO units,

- ethoxylated tri(1-phenylethyl)phenols containing from 2 to 50 EO units,
- propoxylated tri(1-phenylethyl)phenols containing from 2 to 50 PO units,
- ethoxypropoxylated tri(1-phenylethyl)phenols containing from 2 to 50 EO + PO units, and
- ethoxypropoxylated nonylphenols containing from 2 to 100 EO + PO units.

16. Microemulsion according to any one of claims 1 to 15, characterised in that the nonionic surfactants used are chosen from:

- ethoxypropoxylated nonylphenols having 25 EO + PO units,
- ethoxypropoxylated nonylphenols having 30 EO + PO units,
- ethoxypropoxylated nonylphenols having 40 EO + PO units,
- ethoxypropoxylated nonylphenols having 55 EO + PO units,
- ethoxypropoxylated nonylphenols having 80 EO + PO units,
- ethoxypropoxylated tri(1-phenylethyl)phenols having 25 EO + PO units,
- ethoxylated tri(1-phenylethyl)phenol having 16 EO units,
- ethoxylated tri(1-phenylethyl)phenol having 20 EO units,
- ethoxylated tri(1-phenylethyl)phenol having 25 EO

units,

- ethoxylated tri(1-phenylethyl)phenol having 40 EO units,
- ethoxylated di(1-phenylethyl)phenol having 5 EO units,
- ethoxylated di(1-phenylethyl)phenol having 11 EO units, and
- ethoxylated di(1-phenylethyl)phenol having 15 EO units.

17. Microemulsion according to any one of claims 1 to 16, characterised in that when the anionic surfactant is an alkylbenzenesulphonate, the nonionic surfactant is chosen from alkoxylated di(1-phenylethyl)phenols and alkoxylated tri(1-phenylethyl)phenols.

18. Microemulsion according to any one of claims 1 to 17, characterised in that the co-surfactants are chosen from n-butanol, isobutanol (butan-2-ol), n-propanol, isopropanol (propan-2-ol), n-pentanol and its branched isomers, n-hexanol and its branched isomers, cyclopentanol, cyclohexanol, methylcyclohexanols, benzyl alcohol, phenylethyl alcohol, 2-methoxyethanol, 2-ethoxyethanol, 2-isopropoxyethanol, 2-n-butoxyethanol, diethylene glycol monomethyl ether, diethylene glycol monoethyl ether, diethylene glycol mono-n-butyl ether, triethylene glycol monoethyl ether, heptanoic acid and its branched isomers, octanoic acid and its branched isomers, nonanoic acid and its branched isomers and decanoic acid and its branched isomers.

19. Microemulsion according to any one of claims 1 to

18, characterised in that they comprise:

- from 0.1% to 70% by weight of at least one pyrethroid in liquid form, and
- from 2% to 50% by weight of a surfactant system comprising at least one anionic surfactant, at least one nonionic surfactant and at least one co-surfactant, in which the ratio by weight of anionic surfactant/nonionic surfactant is from 15/85 to 85/15 and the ratio by weight of co-surfactant/anionic and nonionic surfactants is from 0.25 to 0.80.

20. Use of the microemulsions according to any one of claims 1 to 19, if appropriate after dilution with water at the time of their use, for controlling insects.

21. Use according to claim 20 for the treatment of crops or the protection of wood.

22. A stable pyrethroid microemulsion, substantially as herein described with reference to any one of Examples 1 to 23 by excluding any comparative examples therein.

23. Use of microemulsion according to claim 22, if appropriate after dilution with water at the time of their use, for controlling insects.

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ABSTRACT

The present invention relates to new stable microemulsions of a pyrethroid characterized in that they comprise:

from 0.1% to 95% by weight/weight of at least one pyrethroid in liquid form;

from 2% to 90% by weight/weight of a surfactant system comprising:

at least one anionic surfactant;

at least one nonionic surfactant;

at least one co-surfactant chosen from the group consisting of aliphatic alcohols, cycloaliphatic alcohols, arylaliphatic alcohols, ether-alcohols and aliphatic carboxylic acids;

and water;

and in that the ratio by weight of anionic surfactant/nonionic surfactant is from 10/90 to 90/10, and the ratio by weight of co-surfactant/anionic and nonionic surfactant is from 0.1 to 1.5.

The microemulsions can be used to control insects, in particular to treat crops and protect wood.